

# The Ground State of a Two-dimensional Lattice System with a Long-range Interparticle Repulsion. Effective Lowering of Dimension.

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It has been shown that effective lowering of dimension underlies ground-state space structure and properties of two-dimensional lattice systems with a long-range interparticle repulsion. On the basis of this fact a rigorous general procedure has been developed to describe the ground state of the systems.

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The two-dimensional (2D) lattice systems with a long-range interparticle repulsion (LSLRIR) are of great interest as they have important physical applications. One of them is the adatom systems<sup>1</sup> with a sufficiently strong interaction between the particles and the substrate. Another field to apply the 2D LSLRIR model is a ‘frozen’ electron phase in 2D or layered narrow-band conductors with a *long-ranged* electron-electron repulsion. This state results from a *suppression* of a narrow-band electrons’ tunneling between host-lattice sites which is produced by the mutual electron repulsion<sup>2</sup> and, therefore, differs principally from a Wigner crystal. (It arises if  $t < \delta u = (a/\bar{r})\bar{u}$ , where  $t$  is the electron bandwidth,  $\delta u$  is the typical change in the energy of a narrow-band electron as it hops between the host-lattice sites,  $a$  is the host-lattice spacing,  $\bar{r}$  is the mean electron separation,  $\bar{u}$  is the mean Coulomb energy per electron). Layered conductors such as cuprates and polycrystal boundaries of the non-linear electroceramic materials<sup>3</sup> as well as art 2D conductors<sup>4</sup> appear to be most favorable for the electron ‘freezing’.

At  $t \ll \delta u$  the 2D - ‘frozen’ - electron phase ground-state space structure is much the same as that of the adatom systems. As far as we know, even in this limit only the one-dimensional (1D) LSLRIR have been studied adequately (ground state<sup>5-7</sup>, thermodynamics<sup>8</sup>). As to the 2D LSLRIR, neither its ground state nor thermodynamics have been explicated. Here we develop a rigorous procedure to describe, in the zero-bandwidth limit, the ground state of the 2D LSLRIR with an *isotropic* pair potential of the interparticle repulsion,  $v(r)$  ( $r$  is a distance between interacting particles). The basis of our consideration is *zero-temperature effective lowering of dimension* in the 2D LSLRIR, which we have found to take place irrespective of a form of  $v(r)$  (within the limits of weak and physically reasonable restrictions) and for any filling factor,  $\rho = N/\mathcal{N}$  ( $N$  and  $\mathcal{N}$  are the total numbers of the particles and host-lattice sites respectively,  $N, \mathcal{N} \rightarrow \infty$ ). We take the term to mean that the ground state of the 2D LSLRIR is an effective 1D LSLRIR whose “particles” are strip-like periodic structures on the 2D host lattice. This enables to describe the ground state analytically, using results of the 1D LSLRIR theory<sup>5-7</sup>.

In the limiting case under consideration the Hamilto-

nian,  $\mathcal{H}$ , of the 2D LSLRIR is of the form

$$\mathcal{H} = \frac{1}{2} \sum_{\vec{r} \neq \vec{r}'} v(|\vec{r} - \vec{r}'|) n(\vec{r}) n(\vec{r}'), \quad (1)$$

where  $\vec{r}$  are radius vectors of sites of the host lattice; it is assumed to be a *triangular* one with  $a = 1$ ;  $n(\vec{r}) = 0$  or  $1$  is the number of particles at a given site; the sum is taken over the whole host-lattice; function  $v(r)$  is assumed to decrease faster than  $r^{-2}$  as  $r \rightarrow \infty$  and to be changed substantially over distances  $\sim \bar{r}$ .

It is reasonable to build up the 2D LSLRIR ground state description around the simplest 2D structures which are stable triangular 2D crystals with one particle per cell and  $\rho = \rho_q \equiv 1/q^2$  (i.e. their primitive translation vectors have a form  $q\vec{a}$ , where  $\vec{a}$  are those of the host lattice). We will call them “ $q$ -crystals”. The stability of the  $q$ -crystals is evident, since it is a triangular lattice that realizes the absolute minimum of the energy of mutual particle repulsion if the particles are free to move. With a view to formulating the general approach to the problem, we start with consideration of small vicinities of  $\rho_q$ . As infinitesimal transformations of the system with the Hamiltonian (1) are impossible, a small change in  $N$  results only in formation of *isolated defects* in a  $q$ -crystal, the space structure of the defects essentially depending on whether they arise on an increase or on a decrease in  $N$ . This fact can formally be expressed by the identity

$$E_g(N \pm \delta N, \mathcal{N}) - E_g(N, \mathcal{N}) = \pm \mu_q^\pm \delta N, \quad (2)$$

$$\delta N/N \rightarrow 0, \quad \delta N/N^{1/2} \rightarrow \infty, \quad (3)$$

where  $E_g$  is the ground-state energy,  $\delta N$  is an arbitrary macroscopically small change in  $N$ . The proportionality coefficients,  $\mu_q^\pm$ , are functions of defects formation energies, interval  $[\mu_q^-, \mu_q^+]$  being the range of the values of the chemical potential,  $\mu$ , at which the  $q$ -crystal exists.

At first glance it would seem that  $\delta N$  should be identified with a number of zero-dimensional defects (“ $\pm$ defectons”), each of them arising as one particle is removed from  $q$ -crystal ( $-$ defecton) or added to it ( $+$ defecton). In such a case  $\mu_q^\pm$  equals the energy of  $\pm$ defecton formation,  $\pm \epsilon_q^\pm$ . The crux of the matter is that this seemingly evident statement is incorrect, as

a rule, due to a *coalescence of defectons of the same "sign"*. What this means is removing from or adding to a  $q$ -crystal *two* particles brings about a bound state of  $-$ defectons or  $+$ defectons ("bidefeton") whose energy is less than  $2\epsilon_q^\pm$  (Fig. 1). We have found out the coalescence by computer calculations, which were carried out for  $v(r) = \exp(-r/R)/r^\beta$  ( $0 < R \leq 20$ ,  $1 < \beta < 12$ ) and  $\rho \geq 10^{-2}$ . They have shown that the phenomenon occurs at any  $q \geq 2$  and for all  $v(r)$  under consideration. The algorithm of the calculations is based on the dipole description of defectons which is as follows.

Each particle displacement in a  $q$ -crystal resulting from  $\pm$ defectons formation can be considered a "dipole" of a sort. This is a pair consisting of the particle shifted and the "antiparticle" located at the host-lattice site left by the particle, the antiparticle "charge" being equal by magnitude but opposite in sign to that of the particle. A  $\pm$ defeton thus comprises a hole ( $-$ defeton) occupying one of the host-lattice sites,  $\vec{r}^-$ , or an added particle ( $+$ defeton) placed in the  $q$ -crystal at a free host-lattice site,  $\vec{r}^+$ , and a system of dipoles, the energy of  $\pm$ defeton formation having the form

$$\epsilon_q^\pm = \min \left( v_\pm(\vec{r}^\pm) \pm \sum_{i=1}^n \hat{\Delta}_{\vec{\xi}_i} v(|\vec{r}_i - \vec{r}^\pm|) + \delta U \right), \quad (4)$$

where  $\hat{\Delta}_{\vec{\xi}} f(\vec{r}) \equiv f(\vec{r} - \vec{\xi}) - f(\vec{r})$  ( $f(r)$  is an arbitrary function);  $\vec{r}_i$  and  $\vec{\xi}_i$  are the  $i$ -th dipole antiparticle site vector number and displacement vector respectively;  $\pm \hat{\Delta}_{\vec{\xi}_i} v(|\vec{r}_i - \vec{r}^\pm|)$  is the energy of interaction between the hole /added particle and  $i$ -th dipole;  $n$  is the number of dipoles;  $v_-(\vec{r}^-) = -2u_q$  is the energy of hole formation ( $u_q > 0$  is the energy of the  $q$ -crystal per particle),  $v_+(\vec{r}^+) > 0$  is that of interaction between the (ideal)  $q$ -crystal and the added particle;  $\delta U > 0$  is the excitation energy of the  $q$ -crystal produced by the displacements of  $n$  particles:

$$\delta U = \sum_{i=1}^n v_q(\vec{\xi}_i) + \frac{1}{2} \sum_{\substack{i,k=1 \\ i \neq k}}^n \hat{\Delta}_{\vec{\xi}_i} \hat{\Delta}_{\vec{\xi}_k} v(|\vec{r}_i - \vec{r}_k|).$$

Here  $v_q(\vec{\xi}) > 0$  is the excitation energy produced by displacement of a  $q$ -crystal particle by host-lattice vector  $\vec{\xi}$ ; the second term is the energy of the dipole-dipole interaction. Minimization in (4) is performed with respect to variables,  $\vec{r}_i$ ,  $\vec{\xi}_i$ ,  $n$ , and  $\vec{r}^\pm$ .

To find the energy of formation of a defect with an arbitrary number of holes/added particles,  $m$ , (let their host-lattice sites be  $\vec{r}_a^\pm$  ( $a = 1, \dots, m$ )) the first two terms in Eq. (4) should be replaced by the corresponding sums over  $\vec{r}_a^\pm$ , and besides, the additional term, the energy of mutual holes/added particles repulsion,  $V_{\text{rep}} = \frac{1}{2} \sum_{a \neq b} v(|\vec{r}_a^\pm - \vec{r}_b^\pm|)$ , should be included, among the variables to be found as a result of the minimization being  $\vec{r}_a^\pm$ .

Using the dipole description, the nature of the coalescence can be clarified. The dipoles of  $\pm$ defeton are always arranged in such a way that they are all *attracted* to the hole/added particle. The bidefeton formation causes an *extra* attraction between the dipoles and holes/added particles, as compared with two isolated defectons. The energy gain exceeds  $V_{\text{rep}}$  and thereby results in the coalescence. This fact is illustrated in Fig. 1. It should be noted that for all  $q \geq 2$  the structures of the attraction cores of the bidefeton (the holes and their nearest dipole surroundings) are much the same. In the case  $q = 1$  the dipoles do not arise (a  $-$ defeton is simply a hole), and hence, the coalescence does not occur.

Formation of a bound state of three  $\pm$ defectons diminishes the energy per particle removed/added still further, and so on to the extent of formation of an infinite *strip* of bound  $\pm$ defectons, which is a periodic 1D structure with a primitive translation vector  $q\vec{a}$  (see Fig. 1). Hence, it is *1D defects*, but not the defectons, which are bound to arise in a  $q$ -crystal as a result of a small variation in  $N$ .

The simplest 1D defect in a  $q$ -crystal is a strip of rarefaction or compression which arises when a  $q$ -crystal part adjacent to a particle line with some primitive translation vector,  $\vec{d}$ , is shifted as a whole relative to the other one by a host-lattice translation vector,  $\vec{\xi}$ . Formation of  $N_s$  strips results in the change,  $\pm \delta \mathcal{N}$ , in the dimensionless volume of the system:  $\pm \delta \mathcal{N} = \pm \sigma L N_s$ , ( $\sigma = 2|\vec{\xi} \times \vec{d}|/\sqrt{3}$ ,  $L \sim N^{1/2}$  is the length of a strip). If  $N_s/N^{1/2} \rightarrow 0$ ,  $N_s \rightarrow \infty$ , the change in the system energy,  $\delta E$ , is proportional to  $\delta \mathcal{N}$ :

$$\delta E = \varepsilon(\vec{d}, \vec{\xi}) \delta \mathcal{N} \quad \varepsilon(\vec{d}, \vec{\xi}) = \sigma^{-1} \sum_{\vec{r}}' \sum_{n=1}^{\infty} \hat{\Delta}_{\vec{\xi}} v(|\vec{r} - n\vec{d}|). \quad (5)$$

Here the accent at  $\Sigma$  means summation over the half-plane  $\vec{r} = l\vec{d} + m\vec{e}$ , ( $l = 0, \pm 1, \dots, -\infty < m \leq 0$ );  $\vec{e}$  is any of the  $q$ -crystal primitive translation vectors differing from  $\vec{d}$ . Only such strips can be relevant to the ground-state properties whose vector parameters,  $\vec{d}$  and  $\vec{\xi}$ , realize the minimum of  $\delta E$ , which equals  $E_g(N, \mathcal{N} - \delta \mathcal{N}) - E_g(N, \mathcal{N})$  (rarefaction,  $\varepsilon < 0$ ) or  $E_g(N, \mathcal{N} + \delta \mathcal{N}) - E_g(N, \mathcal{N})$  (compression,  $\varepsilon > 0$ ). We will call them ' $-$ strips' or ' $+$ strips', depending on whether they result from rarefaction (sign  $-$ ) or compression (sign  $+$ ); their vectors  $\vec{d}$  ('directors') and  $\vec{\xi}$  are denoted here by  $\vec{d}_q^\pm$  and  $\vec{\xi}_q^\pm$  respectively. Our computer calculations based on (5) have shown that the space structure of  $\pm$ strips is the same for all  $q$  and  $v(r)$ :

$$\vec{d}_q^\pm = q\vec{a}_\alpha, \quad \vec{\xi}_q^\pm = \mp \vec{a}_\beta, \quad \alpha \neq \beta. \quad (6)$$

where vectors  $\vec{a}_\alpha$  ( $\alpha = 1, 2, 3$ ;  $|\vec{a}_\alpha| = 1$ ) are the host-lattice primitive translation vectors which form an angle of  $120^\circ$  with one another.

As indicated later,  $\pm$ strips of the same sign *repel* each other at any distances. Hence, the complex strip which result from the defecton coalescence is bound to dissociate to its constituents, simple ones. Noticing also

that breaking  $\pm$ strips into fragments shifted relative to one another increases inevitably the energy of the system (this physically evident statement is completely confirmed by our computer calculations), we can conclude that it is just the  $\pm$ strips which are the above-mentioned 1D defects.

As follows from simple thermodynamic considerations, the coefficients  $\mu_q^\pm$  in Eq. (2) are related to the energy of  $\pm$ strip formation,  $\varepsilon_q^\pm = |\varepsilon(\vec{d}_q^\pm, \vec{\xi}_q^\pm)|$ , by the expression

$$\mu_q^\pm = q^2 \varepsilon_q^\pm + u_q. \quad (7)$$

Lest there be a contradiction to the fact of the defecton coalescence, the energies of  $\pm$ defecton formation are bound to be external to the interval  $[\mu_q^-, \mu_q^+]$ . This can be established by a rather simple reasoning for  $v(r)$  which goes to zero over distances  $R \ll \bar{r} \sim q$ . As  $|\vec{\xi}_q^\pm| = 1$ , from Eq. (5) we have  $\varepsilon_q^\pm \sim (qR)^{-1} u_q$ . On the other hand,  $|\varepsilon_-|$  is comparable with  $u_q$ , and hence,  $\mu_q^- \sim (q/R) u_q \gg |\varepsilon_-|$ . To evaluate  $\varepsilon_q^+$  one should take into account that  $+$ defecton formation significantly decreases the least of the interparticle distances,  $r_{min}$ , as compared with  $\bar{r}$ . Therefore,  $\varepsilon_q^+ \sim v(r_{min}) \gg \mu_q^+ \sim (q/R) v(\bar{r})$ . To make sure that the inequalities,  $|\varepsilon_q^-| < \mu_q^- < \mu_q^+ < \varepsilon_q^+$ , hold irrespective of a form of  $v(r)$  the computer calculations of  $\mu_q^\pm$  based on Eq. (4), (5), and (7) have been carried out in parallel to the computer studies of the coalescence. They have confirmed that the above inequalities are really the case for all  $v(r)$  under consideration and for all  $q \geq 2$ .

The above reasoning shows that at  $|\rho - \rho_q| \ll 1$  the 2D LSLRIR *ground-state* space structure is a kind of a dilute solid solution of  $-$ strips or  $+$ strips (depending on the sign of  $\rho - \rho_q$ ) in the  $q$ -crystal,  $\pm$ strips sharing their primitive translation vector,  $q\vec{a}_\alpha$ , with ‘unperturbed’  $q$ -crystal strips. It should be noted that due to the degeneration caused by the hexagonal symmetry of the  $q$ -crystal (see Eq. (6)) at a given  $\rho$  superstructures can exist which comprise strips with different  $\vec{d}_q^\pm$ . However, these cannot be the ground state, as intersections of the strips inevitably result in an extra increase in the system energy. It can also be shown that the same holds for the mixtures of  $\pm$ strips with the same director but different displacement vectors,  $\vec{\xi}_q^\pm = \mp \vec{a}_\beta$ . To find the arrangement of the  $\pm$ strips with a given director and a given displacement vector one can consider the 2D LSLRIR as an 1D LSLRIR whose ‘particles’ are *particle lines* of the 2D system,

$$\vec{r} = kq\vec{a}_\alpha + l\vec{a}_\beta \quad (k = 0, \pm 1, \pm 2, \dots; \alpha \neq \beta), \quad (8)$$

with integers  $l$  as ‘coordinates’. From this point of view a  $\pm$ strip is a pair of lines (8) which are shifted relative to one another by vector  $(q \mp 1)\vec{a}_\beta$ , while the relative displacement vector of the lines which form an unperturbed strip is  $q\vec{a}_\beta$ .

The line arrangement is governed by the pair potential of line-line interaction,

$$V_q(l_2 - l_1) = \sum_{k=-\infty}^{\infty} v(|kq\vec{a}_\alpha + (l_2 - l_1)\vec{a}_\beta|), \quad (\alpha \neq \beta), \quad (9)$$

where  $l_1, l_2$  are ‘coordinates’ of interacting lines. Simple computer calculations show that due to convexity of  $v(r)$  the pair potential (9) is positive and monotonically decreasing function of  $l$  which also meets the convexity condition,  $F_q(l) \equiv V_q(l) - 2V_q(l+1) + V_q(l+2) > 0$ , over the whole range  $l > 1$  and for all  $q \geq 2$ . It follows herefrom that the arrangement of the lines (8), at least in some vicinity of  $\rho_q$ , is the same as that of the 1D LSLRIR particles, and hence, it obeys the universal Hubbard algorithm<sup>5-7</sup>

$$l_m = [\bar{l}m], \quad \bar{l} = \vartheta/q \quad (10a)$$

where  $\bar{l}$  is the mean line separation,  $\vartheta = 1/\rho$ ,  $l_m$  is the ‘coordinate’ of  $m$ -th line. The algorithm determining the arrangement of  $\pm$ strips can be found directly from Eq. (10a):

$$n_m = [m/c_s^\pm]; \quad q(q \mp c_s^\pm) = \vartheta \quad 0 \leq c_s^\pm \leq 1. \quad (10b)$$

Here  $m$  enumerates the  $\pm$ strips,  $n_m$  is the number of the particle lines between  $m$ -th  $\pm$ strip and  $\pm$ strip with  $m = 0$ ;  $c_s^\pm = N_s^\pm/N_l$  is the concentration of the  $\pm$ strips ( $N_s^\pm$  and  $N_l$  are total numbers of the  $\pm$ strips and the particle lines respectively).

The 2D LSLRIR ground-state space structures (10b) are stable not only in some vicinity of  $\vartheta = q^2$ , but also over the whole range of  $\pm$ strip concentrations,  $0 \leq c_s^\pm \leq 1$ . This is due to the following closely correlated facts, which we (using computer calculations) have found to take place for any  $v(r)$  under consideration: a) zero-dimensional defects (defectons) of a structure described by Eq. (10) coalesce irrespective of a  $c_s^\pm$  value; b) therefore, an infinitesimally small variation in  $c_s^\pm$  produces only 1D defects in the structure; c) their primitive translation vectors turn out to be equal to  $q\vec{a}_\alpha$  for any  $c_s^\pm$ .

At  $c_s^- = 1$  ( $\vartheta = q(q+1)$ ) algorithm (10) determines the stable simple crystal with primitive translation vectors  $q\vec{a}_\alpha, (q+1)\vec{a}_\beta$  ( $\alpha \neq \beta$ ). This can also be considered to be the structure arising at  $c_s^+ = 1$  as a result of compression of the  $q+1$ -crystal. Hence, universal algorithm (10) ( $q = 2, 3, \dots$ ) covers the whole range  $2 \leq \vartheta < \infty$ , expressions (10) holding over the intervals  $q(q-1) \leq \vartheta \leq q(q+1)$ . For each interval there is its own set of directors,  $q\vec{a}_\alpha$ .

The only exception, as our computer calculations have shown, is a vicinity of  $\vartheta = 2$  where the above algorithm fails in the case of slow-diminishing pair potentials  $v(r)$ . Particularly, if  $v(r) = \exp(r/R)/r$  or  $v(r) = 1/r^\gamma$ , this occurs for  $R \geq R_0 \approx 0.38$  or  $\gamma \leq \gamma_0 \approx 4.3$  respectively. The matter is that for  $v(r)$  of such a type the coalescence of  $\pm$ defectons of the simple crystal with  $\vartheta = 2$  (its primitive translation vectors are  $\vec{a}_\alpha, 2\vec{a}_\beta$ , ( $\alpha \neq \beta$ )) leads to formation of 1D defects the primitive translation vector of which,  $4\vec{a}_\alpha$ , is *doubled* in length as compared with

director corresponding to  $q = 2$ . These defects cannot disassociate into simple strips of the above type. Our preliminary results suggest that on interval the  $2 \leq \vartheta \leq 4$  there exists a critical point (its position depends on a form of  $v(r)$ ), at which the 2D LSLRIR ground state undergoes a first-order structure transition with doubling of a spacing,  $2\vec{a}_\alpha \rightarrow 4\vec{a}_\alpha$ . We are going to carry out a detailed study of the situation in a separate paper.

The 2D LSLRIR ground-state dependence of the chemical potential,  $\mu$ , on  $\rho$ , just as it takes place for the 1D LSLRIR<sup>5-7</sup>, is a devil staircase whose steps occur at all rational  $\vartheta$ . Taking into account Eq. (10a), one can represent  $\vartheta$  in a form  $\vartheta = q\bar{l}$  ( $q = 2, 3, \dots$ ), where  $\bar{l} = Q/P$ , and  $P, Q$  are any coprime integers meeting conditions  $q-1 \leq Q/P \leq q+1$ . Thus, the 2D LSLRIR ground state is a set of crystals with  $P$  particles per cell and primitive translation vectors  $q\vec{a}_\alpha, Q\vec{a}_\beta$ ,  $\alpha \neq \beta$ , the crystals with one particle per cell having  $\vartheta = q^2$  or  $q(q+1)$ . Using results of the 1D LSLRIR theory<sup>6,7</sup>, we have found the widths of the devil-staircase intervals,  $\Delta\mu$ , to be related to the line pair potential (9) by an expression

$$\Delta\mu = Q \sum_{m=1}^{\infty} mF_q(Qm-1) > 0 \quad (11)$$

At a given  $q \geq 2$  the expression holds over the interval  $q(q-1) \leq \vartheta \leq q(q+1)$ . It should be noted that  $\Delta\mu$ , similarly to the 1D case, does not depend on the number of particles per cell,  $P$ . In the case of  $q$ -crystal ( $Q = q$ ,  $P = 1$ ) expression (11) coincides with  $\mu_q^+ - \mu_q^-$ , (see Eq. (7)).

The above theory holds over the interval  $1 \geq \rho \geq 1/2$  if one applies it to the holes (empty host-lattice sites) as the particles, the filling factor of holes,  $\rho_h$ , being equal to  $1 - \rho$ . It is evident that the hole space structure corresponding to a given  $\rho_h$  is equivalent to the particle one with  $\rho = 1 - \rho_h$ .

In essence, the effective lowering of dimension and the coalescence of defectons underlying it are caused by discreteness of the system under consideration. Therefore, the phenomena should be expected to exist irrespective of the geometry of a host lattice. Our preliminary studies have confirmed this suggestion, yet they have shown that for an arbitrary host lattice the structure of the 2D LSLRIR ground state turns out to be more sophisticated than in the case of a triangular host lattice. We also have revealed that at non-zero temperatures the lowering of dimension leads to an interplay of a strongly correlated liquid of the thermally fractured 1D defects and an ideal gas of defectons mentioned. This results in a very interesting low-temperature thermodynamics of the 2D LSLRIR. We are going to publish the results concerning these issues in the near future.

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FIG. 1. The coalescence of  $-$ defectons in  $q$ -crystal with  $q = 4$ . Here  $\circ$  denotes host-lattice sites,  $\bullet$  - particles;  $\odot$  - antiparticles;  $\otimes$  - holes;  $\rightarrow$  - dipoles; the dotted lines mark off a single defecton, a bidefeton. The attraction core of the bidefeton consists of dipoles  $D_1, D_2$ , and holes  $H_1, H_2$ . The total energy of attraction  $H_1 \leftrightarrow D_2$  and  $H_2 \leftrightarrow D_1$  exceeds the energy of repulsion  $H_1 \leftrightarrow H_2$ . With an increase of number of removed particles the strip of bound defectons arises, the holes of the strip stringing out along a particle line passing through the sites  $H_1, H_2$ .